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COMPLETE SPECIFICATION

Method of Plasticizing Linear Aromatic Polyesters

We, THE GOODYEAR TIRE & RUBBER COMPANY, a corporation organized under the Laws of the State of Ohio, United States of America, with offices at 1144 East Market Street, Akron, Ohio, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method of plasticizing linear aromatic polyesters.

High molecular weight linear polyesters vary in properties from low melting amorphous substances to high melting readily crystallizable materials. In many instances, these materials cannot readily be plasticized by the usually employed techniques. For example, incorporating the plasticizers in the monomers from which these polyesters are made and then polymerizing the monomers does not give plasticized products, as it does in certain vinyl resin plasticization processes, because the high molecular weight polyesters are prepared by esterification reactions or by the ester interchange method. The materials used as plasticizers would enter into such reactions and actually become a part of the polyester molecule instead of acting as a plasticizer for the polyester. With respect to the linear aromatic polyesters having very high melting points, i.e. above 160° C., they cannot be plasticized by the usual methods of plasticizing high molecular weight materials. For example, such materials cannot be plasticized on a mill or in a Banbury internal mixer by adding the liquid plasticizer to the polymer and masticating at the temperatures available in these machines. These polyesters, being high melting and highly crystalline, and generally possessing rapid rates of crystallization, either do not accept the plasticizer or, before the plasticizer can be incorporated into the polymer, crystallize to form hard materials that cannot be worked in these mixing machines. Heretofore no satisfactory method has existed

for plasticizing all of the various linear aromatic polyesters.

According to this invention high molecular weight linear aromatic polyesters having melting points or softening points above room temperature, and, particularly, crystallizable linear aromatic polyesters having melting points above 160° C., are plasticized by adding plasticizer to the molten polyester and mixing the materials together at a temperature above the melting point of the polyester until a homogeneous mass is obtained. The term "high molecular weight polyesters" is used in this specification and the appended claims to mean those polyesters having an intrinsic viscosity of at least 0.40 when measured at 30° C. in a solvent composed of a 60/40 w/w mixture of phenol and tetrachloroethane. Intrinsic viscosity is used as a measure of the degree of polymerization of the polyester and can be calculated using the Billmeyer extrapolation equation:—

$$[\eta] = \frac{\eta_{sp}}{C} + \frac{\log_e \eta_r}{C}$$

in which $[\eta]$, intrinsic viscosity, is the limit

$$\frac{\eta_{sp}}{C} \text{ as } \eta_{sp} \rightarrow 0$$

$$\eta_{sp} = (\eta_r^{-1})$$

$$\eta_r = \frac{\text{viscosity of solution}}{\text{viscosity of solvent}}$$

and C is the concentration in grams of the polyester per 100 cc. of the solution.

The following example illustrates the process of this invention, the copolymer constituent proportions being given in mol per cent:—

EXAMPLE A.

One thousand and fifty grams of a 60/40 ethylene terephthalate/ethylene isophthalate copolyester were prepared by the ester interchange method. Immediately after the polymerization reaction was completed and while the polyester was still molten 200 grams of a

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plasticizer mixture containing 50% by weight of diethoxyethylphthalate and 50% by weight of butylbenzylphthalate heated to a temperature of about 200° C. were added to the molten polyester and the mixture was stirred for 15 to 20 minutes at approximately 250° C. The polyester-plasticizer mixture was extruded from the reactor and cooled. The resulting composition was flexible, relatively soft and had the general properties of a plasticized resin.

The above example illustrates the invention as applied to a 60/40 ethylene terephthalate/ethylene isophthalate copolyester. The process is also applicable to other linear aromatic polyesters. The term "aromatic polyester" whenever employed in the specification and claims is intended to mean a polyester in which the recurring structural unit contains an aromatic nucleus. Examples of aromatic polyesters are the polyesters derived by the self-condensation of hydroxy acids such as para-(beta-hydroxy ethoxy) benzoic acid, para-(hydroxy methyl) benzoic acid, and para-(beta-hydroxy ethyl) benzoic acid. Further examples are polyesters derived from the condensation of dicarboxylic acids such as terephthalic acid, isophthalic acid, 1,4-diphenoxy benzene-4',4''-dicarboxylic acid, 1,4-bis-(phenoxy methyl)-benzene-4',4''-dicarboxylic acid, (phenoxy methyl)-benzene-4,4'-dicarboxylic acid, phenoxy benzene-4,4'-dicarboxylic acid and diphenoxy alkane dicarboxylic acids with glycols such as ethylene glycol, trimethylene glycol, tetramethylene glycol and hexamethylene glycol. Further examples are polyesters derived from dihydroxy aromatic compounds such as hydroquinone and a dicarboxylic acid. Suitable derivatives of the acids such as the amides, acid chlorides, and the esters such as the methyl, ethyl, propyl, butyl, amyl and phenyl ester can be used. Various copolyesters from these and similar reactants can also be used. The polyesters derived from terephthalic acid and isophthalic acid or ester-forming derivatives thereof with a glycol, and terephthalate-isophthalate copolyesters constitute a preferred class. The invention has particular utility in its application to polymeric ethylene terephthalate and ethylene terephthalate-isophthalate copolymers.

The method has particular value and utility with those high molecular weight linear polyesters having melting points above about 160° C. A preferred group of polyesters to which this invention can be applied is the group of polyesters derived from terephthalic acid or isophthalic acid or mixtures thereof especially the ethylene glycol esters, and particularly those containing 70% or more of terephthalate linkages in the polyester chain.

Any plasticizer can be used in this invention which is compatible with and has plasticizing action on the particular aromatic

linear polyester. In general, it is preferred to use a plasticizer which is liquid at room temperature, but for some applications a material which is a solid at room temperature, but liquid at the melting temperature of the polyester, can be used. It is preferred that the plasticizer be in liquid state when added to the polyester. Representative examples are the other esters of phthalic acid, such as dimethoxyethylphthalate, diethoxyethylphthalate and diethyleneglycol monoethylether phthalate, the glycolate esters of phthalic acid such as methylphthalylmethylglycolate and ethylphthalylethylglycolate, and aralkyl and aromatic esters of dicarboxylic acids, such as butylbenzylphthalate, diphenylphthalate and dibenzylsebacate, tetrahydrofurfuryl esters of dicarboxylic acids, such as tetrahydrofurfuryl adipate and tetrahydrofurfuryl sebacate, the aromatic and mixed aliphatic-aromatic esters of phosphoric acid, such as tricresylphosphate, cresyldiphenylphosphate, and methyldiphenylphosphate, the sulfonamides such as N-ethyl-o-toluenesulfonamide, and N-ethyl p-toluenesulfonamide, and the aralkylethers such as bis-(dimethylbenzyl) ether.

Example A has illustrated the invention as it is applied to preparing a plasticized resin from the polyester immediately after it has been made. While this is a preferred embodiment of the invention, these polyesters can also be plasticized by heating solid polyester to a temperature above its melting point and then adding the plasticizer and mixing it into the polyester. It is preferred to have the plasticizer at a temperature above the melting point of the polyester when the addition is made. This allows for addition of the plasticizer at a faster rate, and avoids any solidification of the materials due to a lowering of the temperature in the mixing vessel by the addition of cold plasticizer.

While certain representative embodiments and details have been shown for the purpose of illustrating the invention, it will be apparent to those skilled in this art that various changes and modifications may be made therein without departing from the scope of the invention, as defined in the appended claims.

Reference is made to copending Applications 1681/56 and 1682/56 (Serial Nos. 805,586 and 805,587) as setting forth inventions in the carrying out of which the process of the present invention may be employed.

WHAT WE CLAIM IS:—

1. A method of plasticizing a linear aromatic polyester which includes the step of adding a plasticizer in liquid form to hot molten polyester and mixing the polyester and plasticizer together until a homogeneous mass is obtained.

2. A method according to Claim 1 in which

the linear aromatic polyester has a melting point above 160° C.

5 3. A method according to Claim 1 or 2 in which the linear aromatic polyester is derived from terephthalic acid and/or isophthalic acid.

10 4. A method according to any of Claims 1 to 4 in which the polyester and plasticizer are mixed together until a homogeneous mass is obtained, and the mixture then cooled until it solidifies.

5. In the process of preparing a linear aro-

matic polyester by an ester interchange reaction followed by condensation reaction, the improvement which comprises adding a plasticizer at a temperature above the softening point of the polyester to the hot, freshly prepared polyester.

6. A method of plasticizing a linear aromatic polyester substantially as set forth and described hereinbefore.

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